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(19) (CA) **CANADIAN PATENT** (12)

(54) MODIFIED FIBERS

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ABSTRACT OF THE DISCLOSURE

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10 novel cellulose-containing fibers are provided herein. The fibers are sulphate pulp fibres, sulphite pulp fibres, semi-chemical pulp fibres, chemi-mechanical pulp fibres, thermo-mechanical pulp fibres or mechanical pulp fibres, or waste paper or waste cardboard fibres or fibre bundles, saw dust, wood chip, shavings, wood wool or synthetic cellulose fibres. The fibres are impregnated with an impregnating agent which is silicon oxide acylates, metal oxide acylates (of, e.g. aluminum, titanium, copper, zinc, antimony, chromium, iron, manganese or zirconium) or a biocidally-active-metal compound of a metal e.g. copper, mercury, chromium, tin and zinc with a salt in a metal organic compound or mixtures of both. These novel cellulose-containing fibers, especially pulp fibers, are rendered suitable as substitutes for, e.g., asbestos fibers, especially in composite materials with cement as a binder.

The present invention relates to cellulose-containing fibres. Such cellulose-containing fibres have novel properties and novel fields of application.

An object of a main aspect of the present invention is to provide fibres which can be used as substitution for inorganic fibres in various types of products, and especially, one aspect of the invention is to provide cellulose-containing fibres which can be used as substitute for asbestos in products conventionally containing asbestos, e.g. asbestos cement products and brake linings, packings, gaskets seals and washers.

10           An object of another aspect of this invention is to provide modified cellulose fibres having an increased dimensional stability, i.e. a minimizing of the tendency of the cellulose-containing fibres to swell under the influence of water. For many purposes where the modified cellulose-containing fibre is to substitute asbestos, it is also desired that it shows a high degree of resistance to deterioration, which means that the modified cellulose-containing fibres should be sufficiently impregnated against biodegradation.

20           By one broad aspect of this invention, cellulose-containing fibres are provided which are selected from the group consisting of sulphate pulp fibres, sulphite pulp fibres, thermo-mechanical pulp fibres and mechanical pulp fibres, or waste paper or waste cardboard fibres or fibre bundles, saw dust, wood chip, shavings, wood wool or synthetic cellulose fibres, the fibres being impregnated with at least one impregnating agent selected from the group consisting of silicon oxide acylates, metal oxide



acylates and a biocidally-active metal compound of a metal selected from the group consisting of copper, mercury, chromium, tin and zinc.

The metal in the metal oxide acylate includes metals selected from the group consisting of aluminum, titanium, copper, zinc, antimony, chromium, iron, manganese, and zirconium.

The non-metallic portion of the biocidally-active metal compound is selected from salts or metal organic compounds or mixtures thereof.

1 salts

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The cellulose containing fibres of one important variant of the present invention are e.g. pulp fibres, sulphate pulp fibers, sulphite pulp fibres, semi-chemical pulp fibres, chemimechanical pulp fibres, thermomechanical pulp fibers and mechanical pulp fibres, for example prepared

total  
pulp

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from soft wood or hard wood, straw or bark. By another variant, the pulp may be bleached or unbleached. By a further variant, the pulp fibers may be in the form of discrete fibers (wet or dry), sheets, rolls, granulates, bales or the like. Important cellulose-containing fibers of other variants of the present invention are waste fibers, for example waste paper or waste cardboard. However, it is also within the scope of other variants of the present invention that the cellulose-containing fibers be fiber bundles, saw dust, wood chip, shavings, wood wool, or synthetic cellulose fibers.

10 By another variant, the impregnating agent is a copper-chromium impregnating agent.

By a variation thereof, the impregnating agent is selected from the group consisting of copper naphthenate copper chromium acetate and copper chromium phosphate.

By a further variant, the metal oxide acylate is a hydrophobizing metal oxide acylate.

By other variants, the hydrophobizing metal oxide acylate is an aluminium oxide acylate or a titanium oxide acylate.

By a still further variant the metal oxide acylate is a biocidal-  
20 ly-active metal oxide acylate.

By a still further variant, the biocidally-active metal oxide acylate is a zinc oxide acylate.

By yet a further variant, the biocidally-active metal oxide acylate and at least one of a hydrophobizing metal oxide acylate and a flame retarding metal oxide acylate.

By a still further variant the fibers also contain a polyelectrolyte.

The cellulose-containing fibers of aspects of the invention are thus characterized by the fact that they are impregnated with at least

one wood preservation agent. In the present context, the term "wood preservation agent" is used in its broad sense and comprises all the well-known types of wood preservation agents, e.g. tar oils, water-borne salts, organic compounds, water repellents, stabilizers, and fire retardants. In other words, quite generally any agent which has been used for or is useful for improving the properties of cellulose-containing fibers or cellulose. The term is intended to comprise here not only such agents as have historically been used for wood preservation purposes, but also agents with similar or improved properties which have not been used so far, but  
10 which are useful in that they are able to combine with cellulose-containing fibers to yield an impregnated product with properties which are improved in desired regards. Such details concerning the wood preservation agents used according to other variants of the present invention are stated below.

The wood preservation agents used according to various variants of the present invention may be of the same kind or similar to the impregnating agents normally used for the impregnation of wood, for example for preservation against biodegradation, for imparting fire resistance, for minimizing moisture content fluctuations, etc.

The typical classes of wood preservation agents of variants  
20 of this invention are:

- (a) tar oils, e.g. creosote, carbolineum (anthracene oil), mixtures of copper salts in carbolinium, combinations of zinc salts and creosote, creosote containing small amounts of arsenic, or different sorts of tars, e.g. wood, peat, or shale tars, or petroleum;
- (b) water-borne salts of e.g. mercury, e.g. mercuric chloride, mixtures of mercuric chloride and copper sulphate with either zinc chloride or sodium fluoride, fluorine, e.g. mixed solutions of sodium fluoride and zinc chloride, Wolman salts (generally considered to be formulations containing fluorine,

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chromium, arsenic and phenol components (FCAP), or fluorine/chromium/arsenic compounds (FCA), zinc, e.g. basic zinc salts, zinc chloride, chromated zinc chloride (CZC), copperized CZC (CCZC), copper, e.g. copper compounds e.g. copper sulphate, copper/chromium/boron (CCB) mixtures, copper/chromium/arsenic (CCA) mixtures, the composition of which is explained in the examples, the so-called CCP mixtures wherein the arsenic contents of CCA has been replaced by phosphorous compounds, e.g. that known by the Trade Mark of BOLIDEN P 50, arsenic, boron, e.g. ammonium borate, ammonium fluoroborates, or trimethylborate, tin, e.g. triorganotin compounds in emulsified or solubilised form e.g. triphenyltin, and tributyltin compounds, e.g. tributyltin oxide, or tin compounds together with silicon, germanium or lead,

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- (C) organic compounds, e.g. nitrated compounds, e.g. nitrated phenol, cresol, xylene, naphthol and anthranol, e.g. dinitro-phenol or dinitro-o-cresol, chlorinated compounds, e.g. chlorophenols, e.g. pentachlorophenol, chloronaphthalenes, chlorobenzenes or hexachlorocyclohexane, e.g. that known by the Trade Mark of LINDANE and that known by the Trade Mark of GAMMEXANE, cyclodiene insecticides, e.g. that known by the Trade Mark of HEPTACHLOR, that known by the Trade Mark of ALDRIN or that known by the Trade Mark of DIELDRIN, organophosphorus, e.g. that known by the Trade Mark of MALATHION, phosphorous trichloride, heavy metal salts of acid phosphate esters, carbamate compounds, or pyrethroids;

or metal salts of organic compounds, e.g. copper pentachlorophenate, copper naphthenate, copper-8-hydroxyquinolate, zinc naphthenate or pentachlorophenate, tin naphthenate or mercury compounds, e.g. ethyl mercury chloride, sulphate, phosphate or acetate or phenol mercury acetate or preferably oleate, or the above-mentioned organo tin compounds in an organic solvent,

d) water-repellent preservatives, e.g. waxes, resins, organosilicon or organoaluminum compounds,

e) fire retardants, e.g. salts or halogenated compounds, e.g. organophosphorus amides, phosphoryl trianilide (PTA), dimeric phosphoric anilanilide (DIP), tris(haloalkyl)phosphate, nitro-containing polyhydric alkanols, linear tertiary phosphine oxide polymers, ammonium polyphosphate, water soluble organic phosphorus esters and polyesters, ammonium derivatives of glyoxylic acid, acid sulphates of aromatic nitroamino compounds, hexachlorocyclopentadiene condensation products, phosphorus- and halogen-containing derivatives of diallyl chlorendate phosphorus oxychloride, alkyl trialkoxy silanes (+ ceric oxide ( $\text{CeO}_2$ )), hexamethylphenyl siloxane (+ prehydrolyzed tetraethyl orthosilicate), lithium-sodium silicate solution, silicone + sodium bicarbonate, alkalimetal glycol monoborates, magnesium oxychloride, tetrabromobisphenol and trixylenyl phosphate, polyethylene and aluminum trihydrate or antimon compounds.

One particular class of compounds which have been found especially interesting as impregnation agents according to a special variant of the present invention either alone or in combination with other wood preservation agents, are the so-called "metal oxide acylates", which is a class of compounds invented by Dr. Jacobus Rinse and disclosed for example in Belgian Patent No. 555,969, Netherlands Patent No. 104,261, U.S. Patent Nos. 3,087,949, 3,243,447, 3,177,238, 3,518,287, 3,625,934,



3,546,262, 3,634,074, and 3,673,229 and Belgian Patent No. 735,548, and U.K. Patent Nos. 1,230,412 and 1,274,718. The metal oxide acylates are believed to be able to react chemically with the hydroxy groups of cellulose-containing fibres, resulting in the attachment of a metal acylate group via an oxygen bridge. Metal oxide acylates may be prepared from a variety of metals, and it is also possible to prepare metal oxide acylates containing more than one metal in the molecule. Hence, metal oxide acylates may be tailored for the present purpose as hydrofobizing agents (aluminum oxide acylates, e.g. aluminum oxide tallate or aluminum oxide stearate or titanium oxide acylates, e.g. titanium oxide versate and silicon oxide acylates), biocidal metal oxide acylates, e.g. copper oxide acylates and zinc oxide acylates, and fire-retardant metal oxide acylates, e.g. antimony oxide acylates. Further interesting metal oxide acylates for the present purpose according to other variants are oxide acylates of chromium, iron, manganese, and zirconium.

By another variant, the fibers are impregnated with a biocidally active heavy metal compound and at least one of a hydrophobizing and a flame retarding metal oxide acylate.

The metal oxide acylates are generally soluble in organic solvents and may be formulated for impregnation as will be described hereinafter.

The impregnation agents used according to various aspects and variants of the invention are preferably so chosen that they are substantially water-insolubly fixed in the fiber structure, if necessary by combination with a separate agent improving the fixation. For example, a water-borne salt impregnation may be combined with a hydrofobization with an effective hydrofobizing agent e.g. aluminum or titanium oxide acylate.

The present invention teaches a process for preparing the impregnated cellulose-containing fibers. The process disclosed herein comprises impregnating cellulose-containing fibers with at least one wood preservation agent by a vacuum and/or pressure impregnation technique. This process may be performed in a manner which is known per se in connection with the wood preservation. The cellulose-containing fibers to be impregnated may be in any desired form, e.g. granulates, sheets, rolls, bales or - when the fibers to be impregnated are waste fibers - simply in the form of paper waste or cardboard waste.

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If the impregnation is performed in the same factory where the impregnated fibers are to be used in a wet process, the defibration can be performed immediately subsequent to the impregnation and without any intermediary drying stages. The impregnated cellulose-containing fiber materials of aspects of the present invention may be defibrated by conventional methods, for example wet defibration in a pulper, or dry defibration.

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The impregnation technique may also be combined with the preparation of paper pulp of any kind, in which case, for example, impregnation with water-borne salts may take place at a stage subsequent to taking up the pulp on the wire but prior to the drying. In this case, the equivalent of a vacuum/pressure treatment may be obtained by pressing the web to a low water content before it is passed through the impregnating bath. Alternatively, impregnation in connection with paper production may of course be performed by impregnating a roll of dried pulp in one of the manners described above.

A further process taught herein for impregnating cellulose fibers especially in connection with the wet preparation of composite material is to carry out the impregnation in situ by means of an oil emulsion which has affinity for the cellulose fibers and in which the wood pre-

servation agent is dissolved in the oil. Thus, for instance, in the production of cement-bound composite materials wherein cellulose fibers as substitute for asbestos or other fibers are used dispersed in water, an oil emulsion of the above-mentioned type may be added to the fiber suspension prior to the addition of the cement.

The impregnation may involve an initial evaporation stage followed by application of the impregnation agent at normal pressure or at super atmospheric pressure. Alternatively the wood preservation agent may be applied dissolved in a low-boiling organic solvent at a temperature immediately below the boiling point of the solvent.

The impregnation for the preparation of the fibers of aspects of the present invention may be carried out according to known procedures, e.g. by spraying, rolling, dipping, squeezing, etc., but the preferred impregnation procedure is one or both of vacuum and pressure impregnation, e.g. impregnation by pressure, in which the impregnating agent is introduced into the material by applying an external pressure, or vacuum impregnation, in which the fibers to be impregnated are first subjected to a vacuum, whereafter the impregnating agent is introduced into the material by releasing the vacuum and optionally applying superatmospheric pressure.

It is also possible to apply alternating pressure-vacuum steps so as to "pump" the impregnating agent through the material.

Depending upon the solubility characteristics of the impregnation agent, the impregnation may be performed by using an impregnating agent dissolved in a volatile solvent at a temperature just below the boiling point of the solvent. The solvent may, for example be methylene chloride, ethylene trichloride, 1,1,1-trichloroethane, fluoro-trichloromethane, or the like. Impregnation by this procedure offers the advantage that the solvent is easily and quickly removed from the impregnated cellulose-containing fibers, thus substantially avoiding the fire hazard of the use of

conventional high-boiling flammable solvents.

The amount of impregnating agent in the impregnated fibers of aspects of the present invention is usually at least 1 percent by weight, calculated on dry fiber weight, and usually at least 5 percent by weight and often 7 - 10 percent by weight.

By another aspect of this invention, a composite material is provided comprising the above described impregnated cellulose-containing fibres and a binder material.

By variants thereof, the binder is an organic polymer, or an  
10 inorganic binder, or a combination of inorganic and organic binder.

By another variant, the composite material includes a poly-electrolyte.

Thus, it has been found, that the impregnation with suitable wood preservation agents imparts, to the cellulose-containing fibers, improved properties with respect to their incorporation in a matrix containing an inorganic binder, e.g. cement. This is believed to be the case especially for impregnation agents which are capable of reducing the inherent capability of the cellulose fibers to attach to each other via hydrogen bonds, which means that an effective test for assessing the  
20 suitability of a wood preservation agent for treatment of cellulose-containing fibers for the present purpose is to form a sheet of the impregnated cellulose fibers, dry the sheet and determine the strength of the sheet. The less bonding between the impregnated cellulose fibers in the resulting sheet, the more inert is the impregnated fiber and, it is believed, the more suitable for incorporation in inorganic binder matrices and other purposes where the fiber is to substitute inorganic fibers, e.g. asbestos.

One advantage of the impregnated fiber of aspects of the present invention is that it can be used as a substitution for asbestos in existing asbestos cement-producing machinery, e.g. the so-called Hatschek and Magnani machines, but the impregnated fibers of aspects

of the present invention in the form of pulp fibers may also e.g. be incorporated in webs formed on a papermaking machine. Thus, one utility of the cellulose-containing fibers of aspects of the present invention is their application as partially or completely inert fibers in the process described in Canadian Patent Application No. 292,361. The fiber according to various aspects of the present invention may be used to substitute, fully or in part, the mineral fibers used in some of the compositions described in the said prior Canadian application. For example, the fibers according to the present invention impregnated

10 with wood-preserving heavy metal compounds may be used for partial or complete replacement of the mineral fibers in the carpet or flooring backing compositions disclosed in the above-mentioned prior patent applications. Other composite materials in which mineral fibers can be wholly or partially replaced with the fibers of the present invention are roofing felt, wall paper, laminated boards, brake linings and other composite materials of the types disclosed in the above-mentioned prior applications, as well as similar composite materials prepared by other methods, including dry methods.

20 The impregnated fibers of aspects of the present invention may also be used as replacement for glass fibers as reinforcing fibers in composite materials with an organic binder matrix, e.g. polyester and epoxypolyester. In this case, a web or plies of the impregnated fibers made by either a dry or a wet method, may be formed using a suitable

B.

binder, analogously to the preparation of webs or plies products of glass fibers.

When the fibers are incorporated in a composite material containing cement as binder, the cement content of the composite material will usually be in the range of 25 - 99 percent by weight, e.g. 50 - 90 percent by weight and often 80 - 90 percent by weight, and the amount of the impregnated cellulose fibers may typically be 1 - 75 percent by weight, more typically 5 - 50 percent by weight, and often 10 - 20 percent by weight of the composite material. The composite material may, in addition to a cement-binder, contain other inorganic material e.g. pozzolana, for example in an amount of 2 - 20 percent by weight, calculated on the weight of the cement, fly ash, etc.

Other composite materials with an inorganic binder which may be made using the impregnated fibers of aspects of the present invention are materials in which the binder is a calcium silicate or plaster, and the relative amounts of these inorganic binders and the impregnated fibers may be the same as stated above in connection with cement-bound composite materials.

Composite materials incorporating the impregnated fibers of aspects of the present invention may also contain both an inorganic binder and an organic binder. Especially suitable organic binders for this purpose are polymer materials constituted by solid discrete particles or fibers having polymer at least at their surfaces, the polymer being a water-insoluble solid synthetic polymer which is film-forming on heating, especially such polymer materials which are disclosed in detail in the prior pending patent applications mentioned hereinabove. The amount of such polymer in composite materials also containing an inorganic binder is usually 1 - 30 percent by weight, calculated on the total weight of the composite material

Accordingly, a process for preparing a composite material using the impregnated fibers of aspects of the present invention may comprise incorporating the impregnated cellulose fiber material dispersed in water. When this process is used for preparing a composite material containing an inorganic binder, e.g. cement, the effective retention and flocculation of the system is, according to aspects of the present invention, obtained by using a polyelectrolyte, in accordance with the principles disclosed in the prior pending patent applications mentioned hereinabove.

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The polyelectrolyte is preferably of the neutral or cationic type. Accordingly, one aspect of the present invention provides a composite material comprising the novel impregnated cellulose-containing fibers and additionally comprising a polyelectrolyte. A polyelectrolyte may also be a useful flocculation agent in composite materials of aspects of the invention which use an organic binder, as taught in the disclosure of the prior pending applications mentioned hereinabove.

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When a polymer which is film-forming on heating is incorporated in the composite material also incorporating an inorganic binder, a suitable method of preparing such composite material comprises subjecting the resulting material, after the shaping in the desired configuration, to a treatment eliciting the film-forming properties of the polymer. The treatment eliciting the film-forming properties of the polymer may be performed after the curing of the inorganic binder, or the treatment eliciting the film-forming properties of the polymer may be performed prior to curing of the inorganic binder, and, subsequently to the eliciting of the film-forming properties of the polymer, the amount of water necessary for curing the inorganic binder may be added, whereafter the final curing may be performed. Another possibility is to combine curing of the inorganic binder and eliciting of the film-forming properties of the polymer in one treatment, for example in an autoclave, depending

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upon the particular binder and polymer used.

When composite materials using the impregnated fibers of aspects of the present invention and with an inorganic binder by a wet method, another possibility for obtaining improved dispersion of the impregnated fibers is to use an oil as dispersing aid, possibly combined with the use of a polyelectrolyte. The oil may suitably be a non-drying oil which may be added to the fibers in the form of an emulsion.

10 In the present context, the term "hydrophobizing agent" is intended to designate not only agents which impart true hydrophobicity to the treated fibers, but also agents which change the properties of the fibers in direction from hydrophilicity towards hydrophobicity.

In the present context, the term "cement" is intended to designate both portland cement types and the other inorganic cement types."

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The following examples teach various aspects and variants of

this invention.

Example 1.

Unbleached sulphate cellulose fibers in sheet form were impregnated with a CCA agent that known by the Trade Mark BOLIDEN K-35 (composition: arsenic, chromium and copper compounds in quantitative ratios corresponding to  $As_2O_5$ :  $34.0\% \pm 2\%$ ,  $CrO_3$ :  $26.6\% \pm 1.5\%$ ,  $CuO$ :  $14.8 \pm 1\%$ ,  $H_2O$ :  $26.6\% \pm 4\%$ ) in two different ways:

- 10 I. The specimen was evacuated to about 60 mm Hg with a water jet air pump and was left for 20 minutes in the impregnating liquid, whereafter the pressure was raised to atmospheric pressure and the specimen was left for a further 20 minutes.
- II. The specimen was evacuated to approximately 60 mm Hg, and the pressure was again raised to atmospheric pressure. This cyclis was repeated 20 times within 20 minutes, whereafter the specimen was left for a further 20 minutes at atmospheric pressure in the impregnating liquid.

The water content of the fibers impregnated according to method I or II was determined by weighing during drying until constant weight at  $105^\circ C$ .

20 The copper, chromium and arsenic contents were determined in the dried specimens. A known quantity of impregnated fibers of specimens I and II were beaten, that is dispersed in water, by means of a blender. Specimens were taken out for washing out experiments. Washing out experiments were performed on the beaten fibers impregnated according to method I or II by the following two methods:

- A. Washing with hot water ( $30^\circ C$ ) for 2 hours under simple stirring with a propeller, the fiber concentration being approximately 2 g/liter water.

B. washing at 20 C for 24 hours with a calcium hydroxide solution at pH 12.0 under slow stirring with a propeller, the fiber concentration being approximately 10 g/liter solution.

After the washing experiments, copper, chromium and arsenic contents were determined in both the washing liquids and the washed fibers.

The water contents in specimens I and II and the results of weighing of fibers are listed in the below Table I.

The results of the determinations of the copper, chromium and arsenic contents are listed in the below Table II. The figures are in mg metal per g dry fiber used.

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Table I.

Fibers impregnated according to	Method I	Method II
Water content in fibers	57.1%	58.9%
Beating of specimens (moist)	100 g	50 g
in water	in 200 ml	in 500 ml

In diluting the beaten specimens for the washings, there was corrected for the initial water content of the specimens, and hence, the below-listed concentrations of fibers in washing liquid represent dry fibers.

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Fiber concentration in the washing experiment.

Washing A	2.21 g/1000 ml	2.12 g/1000 ml
Washing B	5.36 g/500 ml	5.14 g/500 ml

Table II.

Content of Copper, Chromium and Arsenic in the Fibers.

Method of impregnation	Copper		Chromium		Arsenic	
	I	II	I	II	I	II
Contents in mg/g in unwashed, impregnated fibers	(13.41) (13.75) 13.6	(13.17) (13.15) 13.2	15.67 16.33 16.0	16.81 15.72 16.3	26.12 26.26 26.2	27.52 25.12
Washed out according to method A, %	24	13	41	25	29	25
Content in fibers, determined after washing according to method A, %	76	87	59	75	71	75
Washed out according to method B, %	0.8	1.4	33	23	4	5
Content in fibers, determined after washing according to method B, %	99.2	98.6	67	77	96	95

$$\frac{13.2}{1.325} = 10.03$$

$$\frac{0.1329}{1.009} = 0.1317$$

The determination of the copper, chromium and arsenic contents in the fibers shows that the fibers were impregnated equally according to the two methods, and that there were the same proportions between copper, chromium and arsenic in the fibers as in the impregnating liquid. The total impregnation corresponds to an uptake of salts of 8 - 9% of the weight of the fibers.

10 In the washing experiments with water according to method A, part of the copper, chromium and arsenic contents in the fibers was washed out, mostly from the fibers impregnated according to method I.

In the washing experiments with calcium hydroxide solution according to method B, practically no copper and little arsenic were washed out, whereas approximately as much chromium was washed out as in the washing experiment A. As regards chromium, again most was washed out from the fibers which were impregnated according to method I. As regards copper and arsenic, the difference in washing out from the fibers impregnated according to method I or II was so little that it was within the uncertainty of the experiment.

20 Sheets of sulphate cellulose fibers impregnated with Boliden K 33 in the manner described above were defibrated in water to yield 1/2% suspension. The defibration required about 50% more beating time than the defibration of corresponding untreated sheets. After the defibration, the suspension was converted into sheets on a laboratory sheet former and dried in an oven at 100°C. After the drying, the resulting sheets showed much less strength than corresponding sheets made from untreated starting fibers: the fibers of the sheets made from the impregnated material could easily be drawn from each other and showed virtually no coherency except that resulting from the entangling.

30 Example 2.

Scanning Electron Microscopy (SEM) on Impregnated Fibers.

various sorts of fibers were impregnated with various impregnation agents according to various methods, as stated in the below scheme, whereafter SEM was performed on the fibers and the contents of S, Ca, Cr, Cu and As were determined by X-ray analysis.

The determinations show that there is no significant difference between the degree of impregnation at the middle of the fibers, at the surface or in between, which indicates that the impregnating agent penetrates into and is evenly distributed in the cell and not only impregnates the surface.

- 10 Experiments 6 and 7 show the effect of pressure impregnation. Experiments 4 and 6 show that the impregnation is improved if the specimen is evacuated before the pressure influence, and the experiments 1 and 4 indicate that the impregnation is improved to a higher extent by application of longer acting evacuation than by application of a higher pressure after the evacuation.

Fiber	Impregnating agent	Impregnating process	SEM Determination. Number of atoms per unit determined at the surface of the fiber at the middle and in between.				
			S	Ca	Cr	Cu	As
1. Unbleached sulphate	Boliden K 33 (0.64%)	Vacuum (60 mm Hg) for 20 minutes - atm. pressure for 20 minutes	middle 256 inbetween 345 surface 446	396 426 443	1480 1733 1722	830 916 958	486 598 612
2. Semichemical beech cellulose	Boliden K 33 (0.64%)	Vacuum (60 mm Hg) for 15 minutes - 10 kg/cm <sup>2</sup> for 60 minutes	middle 812 inbetween 957 surface 756	181 244 194	589 833 930	330 420 558	216 210 4
3. Unbleached sulphate	Gori 22 "grøn kobber"*	Vacuum (60 mm Hg) for 15 minutes - 10 kg/cm <sup>2</sup> for 60 minutes	middle 699 inbetween 628 surface 553	631 695 581	0 7 0	820 2632 3210	0 0 0
4. Unbleached sulphate	Boliden K 33 (0.64%) + 1% Mulgofen EL 719	Vacuum (60 mm Hg) for 15 minutes - 10 kg/cm <sup>2</sup> for 60 minutes	middle 183 inbetween 157 surface 193	307 348 396	394 504 380	278 304 628	110 170 136
5. Corrugated paper	Boliden K 33 (0.64%) + 1% Mulgofen EL 719	Vacuum (60 mm Hg) for 15 minutes - 10 kg/cm <sup>2</sup> for 60 minutes	middle 111 inbetween 99 surface 92	114 140 124	938 947 876	942 1108 738	288 278 240
6. Unbleached sulphate	Boliden K 33 (0.64%) + 1% Mulgofen EL 719	Submersed for 20 minutes	middle 116 inbetween 102 surface 92	288 368 353	243 279 290	78 78 106	44 62 130
6a. Unbleached sulphate	Boliden K 33 (0.64%) + 1% Mulgofen EL 719	Submersed for 20 minutes	middle 150 inbetween 163 surface 193	331 366 349	283 297 283	90 88 60	200 2 96
7. Unbleached sulphate	None	Not treated	middle 247 inbetween 200 surface 260	347 424 428	0 8 11	0 14 0	0 0 0

\* (25% solution of copper naphthenate in white spirit)

\*\* (Mulgofen is a trade mark; emulsifier based on polyethoxylated alcohols)

Example 3.

Strips of filter material made of bleached sulphate cellulose were dipped for one second in a solution of 7 parts by weight of FRIGEN S11 (the trade mark for a brand of fluorotrichloromethane) and 1 part by weight of metal oxide acylate containing 30% of white spirit. The strips were dried in an oven at 100°C for one hour. The metal oxide acylates used were titanium oxide stearate (D-14-00), zinc oxide versate (E-12-80, containing only 20% of white spirit), aluminum oxide phthalate (C-10-70), aluminum oxide stearate (C-14-70) and aluminum oxide stearate/phthalate (C-10/14-70),

10 all supplied by MOACO S.A., Echallens, Switzerland. The impregnated paper strips, with the exception of the strips treated with zinc oxide versate, showed hydrophobicity, especially the specimen impregnated with titanium oxide stearate, and all the impregnated paper strips, including the zinc oxide versate-treated strip, showed less elongation upon dipping in water than the controls.

The strips were defibrated by beating in water in a blender. The zinc oxide versate-treated strip was defibrated as easily as the untreated strips, whereas about 50% longer treating time was required for the defibration of the other metal oxide acylate-treated strips. After the de-

20 fibrillation, the pulp of aluminum oxide phthalate-treated fibers was converted into a sheet in a laboratory sheet former, and the sheet was dried in an oven at 100°C for one hour. The resulting dried sheet showed considerably less strength than a corresponding sheet made of untreated fibers, indicating little or no chemical bonding between the fibers.

Example 4.

The sheet of BOLIDEN K-35 impregnated fibers made in a laboratory sheet former and thereafter dried (vide Example 1) was dipped into a solution of 1 part of titanium oxide stearate (D-14-00 from MOACO S.A.) in 7 parts of FRIGEN S11 for one second. Thereafter, the fibrous mass was dried in



an oven at 100°C for one hour. After the drying, the material showed excellent hydrophobic properties, in contrast to the BOLIDEN K-33-impregnated fibers which had not been treated with titanium oxide stearate.

#### Example 5.

10 Sulphate cellulose pulp was impregnated with BOLIDEN K 33 as described in Example 1, method I. The impregnated fibers had a salt content of 5% by weight. The resulting impregnated sheet of fiber pulp was defibrated in a blender and, to the defibrated suspension in a quantity corresponding to 40 g of dry material consisting of impregnated fibers was added 160 g of cement (super rapid). The quantity of water present was such that the total content of dry matter, cement + fibers, was approximately 1/2% by weight. The suspension was poured into the chest of a sheet former, and immediately before the water was suctioned off, a polyelectrolyte was added in a quantity of 0.04%, calculated on the dry matter. The polyelectrolyte was, one run, the polyelectrolyte known by the Trade Mark PRODEFLOC CL and, in another run, the polyelectrolyte known by the Trade Mark PRODEFLOC N2M. By suction of the water, a sheet was produced having a thickness of approximately 3 mm. The sheet was left for curing in a plastic bag which was closed so that no water could evaporate from the specimen. After 20 curing, the board was judged to have a tensile strength about equal to that of conventional asbestos cement.

#### Example 6

Using the same process as described in Example 5, but using 80 g of impregnated fibers, calculated as dry matter, instead of 40 g of impregnated fibers, a board having a thickness of 12 mm was produced.

C.

#### Example 7

Using the same process as described in Example 5, but using 160 g of dry matter consisting of impregnated fibers instead of 40 g of dry matter consisting of impregnated fibers, a board having a thickness of 20 mm was produced, which board had the character of a fiber board. The dewatering was in this example somewhat slower than in Examples 5 and 6.

#### Example 8

The process described in Example 5 was followed, but additionally, 5% by weight of epoxypolyester powder, calculated on the total dry matter, was added together with the cement. After one day of curing in a plastic bag, 10 the board was removed and placed for drying at 100°C in an oven, and when the board had dried to constant weight, the temperature was raised to 200°C, and the board was kept for 2 minutes at 200°C. After cooling, the board was moistened again so that the cement could continue curing. After curing, the board had an excellent tensile strength and a tight, smooth and beautiful surface. A similar experiment was performed using a smaller amount of water, viz. a water/cement ratio of approximately 50. A similar excellent result was obtained.

#### Example 9

Dry sulphate cellulose pulp (approximately 5 g) was soaked with colourless 20 SOLIGNUM ULTRA (the trade mark for a wood preservation agent based on oil binders and fungicides) by dipping, excess impregnating liquid was squeezed out manually, and the pulp was immediately thereafter beaten in water in a blender. The defibrated pulp was dewatered by manual pressing and was mixed with approximately 20 g of cement (super rapid) to which was added about 10 g of water. The fibers were easily dispersed homogeneously in the cement and the resulting pulp was soft and plastic without lumps.

C<sub>1</sub>

Example 10.

Dry sulphate cellulose pulp (about 5 g) was soaked with silicon oil by dipping, excess oil was squeezed out manually and the pulp was immediately thereafter beaten in water in a blender. The pulp was easily defibrated, and the fibers were dewatered by manual pressing and were blended with approximately 20 g of cement (super rapid), to which was added approximately 10 g of water. The fibers were easily dispersed homogenously in the cement matrix, and the resulting pulp was soft and plastic without lumps.

Example 11.

- 10 A piece of cardboard (approximately 5 g) was soaked with colourless "BON-DEX" (the trade mark for a wood preservation agent based on oil binders and fungicides) by dipping, excess impregnation liquid was squeezed out manually, and the pulp was immediately thereafter beaten in water in a blender. The pulp was easily defibrated, the fibers were dewatered by manual pressing and were mixed with approximately 20 g of cement (super rapid), to which was added approximately 10 g of water. The fibers were easily dispersed homogenously in the cement matrix, and the resulting pulp was poured into a mould and left for drying. After 5 days of curing, the reinforced cement board had a thickness of approximately 1 cm, had high  
20 strength, and in the microscope, fractured surfaces showed homogenous distribution of the fibers.

Example 12.

Sulphate cellulose pulp was impregnated with BOLIDEN K 33 as described in Example 1, method I. The impregnated fibers had a salt content of 5% by weight. The resulting impregnated sheets of fiber pulp were defibrated in a blender and the defibrated suspension in a quantity corresponding to 8.5 g of dry material

C.

10 consisting of impregnated fibers was admixed with 66.5 g of cement (rapid), 30 g of amorphous silica (fly ash from the production of ferrosilicon) and 5 g of a powder of epoxypolyester (55% by weight) applied on 43% by weight of  $TiO_2$ /2% by weight of  $BaSO_4$ , particle size 30 - 80  $\mu$ . Water was added so that the concentration of dry matter in the resulting suspension was 4%. The suspension was poured into the chest of a laboratory sheet former, and immediately prior to suctioning off the water, 0.5% of Prodefloc N2M (a polyelectrolyte) was added. By suctioning off the water, a sheet was formed which was allowed to cure for about 12 hours. Thereafter, the sheet was kept for 1 hour in an oven at 100°C and subsequently for about 15 minutes at 220°C. The resulting board had a smooth surface and showed uniform fiber distribution.

The impregnated cellulose-containing fibers of aspects of the present invention may thus be used for a wide range of applications in which their modified and improved properties are desired.

THE METHODS OF THE INVENTION IN WHICH AN EXCLUSIVE  
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Cellulose-containing fibres selected from the group consisting of sulphate pulp fibres, sulphite fibres, semi-chemical fibres, chemi-mechanical pulp fibres, thermo-mechanical pulp fibres and mechanical pulp fibres, or waste paper or waste cardboard fibres or fibre bundles, saw dust, wood chip, shavings, wood wool or synthetic cellulose fibres, said fibres being impregnated with at least one impregnating agent selected from the group consisting of silicon oxide acylates, metal oxide acylates and a biocidally-active metal compound of a metal selected from the group consisting of copper, mercury, chromium, tin and zinc.

2. The cellulose-containing fibres of claim 1 wherein said metal oxide acylates include metals selected from the group consisting of copper, zinc, antimony, chromium, iron, manganese, and zirconium.

3. The cellulose-containing fibres of claim 1 wherein the non-metallic portion of the biocidally-active metal compound is selected from salts or metal organic compounds or mixtures thereof.

4. The cellulose-containing fibres of claims 1, 2 or 3 wherein said fibres are in one of the following forms:

- (a) dry discrete fibres
- (b) wet discrete fibres
- (c) sheets
- (d) rolls
- (e) bales
- or (f) granulates

5. cellulose-containing fibres of claims 1, 2 or 3 wherein said fibres are in one of the following forms:

- (a) dry discrete fibres
- (b) wet discrete fibres
- (c) sheets
- (d) rolls
- (e) bales

or (f) granulates

and wherein said fibres are in the form of fibre bundles.

6. The cellulose containing fibres of claims 1, 2 or 3 wherein said fibres are in one of the following forms:

- (a) dry discrete fibres
- (b) wet discrete fibres
- (c) sheets
- (d) rolls
- (e) bales

or (f) granulates

and wherein said fibres are of saw dust, wood chips, wood wool or synthetic cellulose.

7. The cellulose-containing fibres of claims 1, 2 or 3 wherein said impregnating agent is a copper-chromium impregnating agent.

8. The cellulose-containing fibres of claims 1, 2 or 3 wherein said impregnating agent is selected from the group consisting of copper naphthenate, copper chromium acetate, and copper chromium phosphate.

9. The cellulose-containing fibres as claimed in claims 1, 2 or 3 wherein said metal oxide acylate is a hydrophobizing metal oxide acylate.

10. The cellulose-containing fibres as claimed in claims 1, 2 or 3 wherein said metal oxide acylate is an aluminium oxide acylate.

11. The cellulose-containing fibres as claimed in claims 1, 2 or 3 wherein said metal oxide acylate is a titanium oxide acylate.

12. The cellulose-containing fibres as claimed in claims 1, 2 or 3 wherein said metal oxide acylate is a biocidally-active metal oxide acylate.

13. The cellulose-containing fibres as claimed in claims 1, 2 or 3 wherein said metal oxide acylate is a zinc oxide acylate.

14. The cellulose-containing fibres as claimed in claims 1, 2 or 3 wherein said fibres are impregnated with a biocidally-active metal oxide acylate and at least one of a hydrophobizing metal oxide acylate and a flame retarding metal oxide acylate.

15. The cellulose-containing fibres as claimed in claims 1, 2 or 3 also containing a polyelectrolyte.

16. A composite material comprising (A) the cellulose-containing fibers of claims 1, 2 or 3 and (B) a binder.

17. A composite material comprising (A) the cellulose-containing fibers of claims 1, 2 or 3 and (B) an organic polymer binder.

18. A composite material comprising (A) the cellulose-containing fibers of claims 1, 2 or 3 and (B) an inorganic binder.

19. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a combination of an inorganic and an organic binder.

20. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder, wherein said fibres are in one of the following forms:

- (a) dry discrete fibres
- (b) wet discrete fibres
- (c) sheets
- (d) rolls
- (e) bales
- or (f) granulates.

21. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder wherein said fibres are in one of the following forms:

- (a) dry discrete fibres
- (b) wet discrete fibres
- (c) sheets
- (d) rolls
- (e) bales
- or (f) granulates.

and further wherein are in the form of fibre bundles.

22. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder, and wherein said fibres are in one of the following forms:

- (a) dry discrete fibres
- (b) wet discrete fibres
- (c) sheets



or (f) bales  
granulates

and further wherein are of saw dust, wood chips, wood wool or synthetic cellulose.

23. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder and wherein said impregnating agent is a copper chromium impregnating agent.

24. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder and wherein said impregnating agent is selected from the group consisting of copper naphthenate copper chromium acetate and copper chromium phosphate.

25. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder and wherein said metal oxide acylate is a hydrophobizing metal oxide acylate.

26. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder and wherein said metal oxide acylate is an aluminum oxide acylate.

27. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder and wherein said metal oxide acylate is a titanium oxide acylate.

28. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder and wherein said metal oxide acylate is a biocidally-active metal oxide acylate.

29. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder and wherein said metal oxide acylate is a zinc oxide acylate.

30. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder and wherein said fibres are impregnated with a biocidally-active metal oxide acylate and at least one of a hydrophobizing metal oxide acylate and a flame retarding metal oxide acylate.

31. A composite material comprising (A) the cellulose-containing fibres of claims 1, 2 or 3 and (B) a binder and also containing a polyelectrolyte.

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